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The CO₂ system in a Redfield context during an iron enrichment experiment in the Southern Ocean

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Abstract

In November 2000, a second iron enrichment experiment (EisenEx) was carried out in the Southern Ocean. Iron was added on the 8th of November in the centre of an eddy at 21°E, 48°S. During the cruise, the carbonate parameters dissolved inorganic carbon (DIC), fugacity of CO₂ (*f*CO₂) and pH on the hydrogen ion scale (pH_T) were determined from water samples from both inside and outside the iron fertilized patch. Before the start of the experiment, the surface properties of the eddy were quite uniform with respect to the carbonate system and representative of the High Nutrient Low Chlorophyll (HNLC) regions in the Southern Ocean. The response of the carbon dioxide system to the initial ≈ 4 nM iron (Fe) infusion and to two subsequent reinfusions at 15 m depth was measured every day during the study. The changes in the carbon dioxide system and major nutrients were strongly influenced by the meteorological conditions with a rapid succession of calm, often sunny spells and storm force winds during the 21 days of experiment. Twenty days after the first Fe-infusion, the maximum changes of the carbonate parameters in surface waters of the patch relative to outside patch were $-15 \mu\text{mol kg}^{-1}$ in DIC, $-23 \mu\text{atm}$ in *f*CO₂, $+0.033$ units in pH_T, $-1.61 \mu\text{M}$ in nitrate and $-0.16 \mu\text{M}$ in phosphate in a mixed layer of 80 m depth. In addition to the daily measurements, several transects were made across the patch that showed a response of the carbonate system to the influence of iron, concomitant with a response in nutrients and chlorophyll. The relative changes in dissolved inorganic carbon to nutrient concentrations inside the patch during the experiment give N/P=12, C/P=82, C/N=5.9, C/Si=2.9 and N/Si=0.5. The effect of the influx of atmospheric CO₂ on the DIC inventory was small with values between 0.05 and 0.10 $\mu\text{mol kg}^{-1} \text{ day}^{-1}$, and did not significantly affect these ratios. Although the observed change in DIC in the Fe-enriched surface waters was lower than in the

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previous Fe-enrichment experiments, the equivalent biological C-uptake of 1.08×10^9 mol C across the patch after 20 days was significant due to the large horizontal dispersion of the patch. The ratio of biological carbon uptake to Fe added ($C_{\text{biological uptake}}/Fe_{\text{added}}$) was 2.5×10^4 mol mol⁻¹.

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Keywords: Southern Ocean; Iron enrichment; Meteorological conditions; Carbon dioxide; nutrients; Redfield ratios

1. Introduction

In three vast oceanic regions (the Southern Ocean, the North Pacific and the Equatorial Pacific), large stocks of major nutrients such as nitrate, phosphate and silicate are available but phytoplankton growth and therefore the biological pump of CO₂ are generally sub-optimal. This is the well-known paradox of the High Nutrients Low Chlorophyll (HNLC) regions. Martin and Fitzwater (1988) suggested that the lack of iron in these areas could limit the phytoplankton growth. Then, Martin (1990) hypothesized that large-scale iron fertilization of the HNLC regions would remove CO₂ from the atmosphere and would sequester it into the deep ocean. This would in turn reduce the greenhouse effect. The “iron hypothesis” was indeed confirmed by in vitro enrichment experiments using incubation bottles (Martin and Fitzwater, 1988; De Baar et al., 1990). However, these experiments were widely discussed (Banse, 1990; Broecker, 1990; Miller et al., 1991; Kurz and Maier-Reimer, 1993), because they did not mimic the open ocean conditions and excluded parameters such as grazing by zooplankton, sinking of particles to the aphotic layer and advection. However, natural iron (Fe)-fertilization (Martin et al., 1994; De Baar et al., 1995; De Baar et al., 1997; Blain et al., 2000) as well as mesoscale in situ experiments (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2003) revealed unambiguously that phytoplankton growth was stimulated by iron enrichment.

In parallel, it has also been shown that the amount of available iron affects the ratio of algal uptake of silicic acid to that of nitrate and phosphate (De Baar et al., 1997; Boyle, 1998; Hutchins and Bruland, 1998; Takeda, 1998). Moreover, variation from the global mean “Redfield” ratio of N/P of about 15:1 (Fanning, 1992), as have been observed in Southern Ocean

waters, may be directly related to Fe supply (De Baar et al., 1997).

During the IronEx I experiment, the effects of algal growth on CO₂ uptake remained low compared to the potential for uptake of CO₂ in the nutrient replete surface waters of the Equatorial Pacific Ocean, since iron fertilized waters were subducted within 4–5 days (Martin et al., 1994; Watson et al., 1994). The IronEx II experiment provided substantial CO₂ uptake (Coale et al., 1996; Cooper et al., 1996; Millero et al., 1998; Steinberg et al., 1998) and it was suggested that, if the Southern Ocean could be similarly influenced, large-scale increases in the iron supply could lower the atmospheric CO₂ concentration by 6–21% based on models of enhanced nutrient utilization (Cooper et al., 1996). The SOIREE experiment demonstrated the occurrence of iron limitation of algal growth in the Southern Ocean (Boyd et al., 2000). After 13 days, approximately 1.1×10^8 mol of carbon had been incorporated into organic matter across the patch (Watson et al., 2000; Bakker et al., 2001). However, the fate of SOIREE bloom could not be ascertained during the 13-day experiment. Knowledge of this fate is crucial for the CO₂ budget. If biomass is respired again in the surface layer by zooplankton and bacteria, no net removal of CO₂ from the atmosphere occurs. However, if the organic matter leaves the surface layer, the equivalent CO₂ amount is removed from the atmosphere for thousands of years.

A large part of the Southern Ocean consists of a broad eastward flowing ring of water, the Antarctic Circumpolar Current (ACC). One of the fronts in the ACC, the Antarctic Polar Front (APF), separates the Polar Frontal Zone (PFZ) to the north from the Antarctic Zone. The purpose of the EisenEx experiment was to determine if phytoplankton of the ACC is iron-limited in spring, to compare the reaction and the evolution of the pelagic ecosystem after fertilization to that in SOIREE in austral autumn and to follow the

evolution of the bloom over time under stormy spring conditions (Smetacek, 2001).

During the 21 days of experiment, we measured vertical profiles of dissolved inorganic carbon (DIC) concentration and the fugacity of carbon dioxide ($f\text{CO}_2$) inside and outside the iron enriched waters (inside and outside “the patch”) in order to study the changes in the carbon system due to iron fertilization. We also continuously measured DIC, $f\text{CO}_2$ and pH_T (pH on the hydrogen ion scale) during the different surface water mappings of the patch in order to study the spatial changes for these parameters.

In the present paper, we firstly detail the patch deployment, as well as the data acquisition and data analysis for the carbonate parameters. Secondly, we focus on the reaction and evolution of the carbonate system under contrasting meteorological conditions during the 21 days of the experiment. In Section 3.4, the changes in DIC are compared to the changes in major nutrients such as nitrate, phosphate and silicate in order to study the Redfield ratios. In Section 3.5, the impact of CO_2 air–sea exchange on these ratios is evaluated and discussed. Finally, we established the biological carbon uptake within the patch and related it to the Fe input.

2. Materials and methods

2.1. Patch deployment

The experiment was performed in the Atlantic sector of the Southern Ocean at 21°E , 48°S in austral spring (6–29 November 2000) during cruise Ant XVIII/2 of R.V. *Polarstern*. The core of an eddy originating from the Southern Polar Front (Strass et al., 2001) was selected after a 750-km surveying transect along the 20°E meridian between the Subantarctic front at 45°S and the Antarctic zone at 52°S . This eddy provided a stable water mass with favourable chemical, biological and physical conditions for the experiment (Smetacek, 2001). In the centre of the eddy marked with a drifting buoy, an area of about 50 km^2 was enriched with iron (Fe(II) from dissolution of FeSO_4 in acidified seawater). This iron sulphate solution, containing a constant ratio of the inert tracer sulphur hexafluoride (SF_6), was released during 15 h in the mixed layer, at a depth

of $16 \pm 2\text{ m}$ in the wake of the ship’s propeller in order to avoid the escape of volatile SF_6 into the atmosphere and to ensure that the tracer and iron were rapidly mixed throughout the mixed layer. The first iron fertilization resulted in an ambient surface water concentration of dissolved iron of $4.5 \pm 3\text{ nM}$ (Croot and Laan, 2001). The first Fe-infusion of the EisenEx experiment was initiated at 17:20 GMT on the 7th of November 2000 and ended at 6:45 GMT on the 8th of November. All times in this paper are relative to 0:00 GMT on 8 November 2000, which was taken as the start of the experiment ($t=0$). Two re-infusions of iron were made on days 7 and 16 of the experiment to maintain the elevated iron concentrations within the Fe-enriched water body (“the patch”). Here, day 7 indicates the seventh day after the first iron addition ($t=7-8$).

2.2. Ship’s surface water supply

The ship’s water supply provided large volumes of water from 12 m depth for continuous sampling of SF_6 , DIC, $f\text{CO}_2$ and pH_T . The temperature difference between the ship’s inlet and the laboratory outlet, warming by an average of 0.2°C (standard deviation of 0.1°C for 2362 points), was monitored and corrected for with the relationship of Takahashi et al. (1993).

2.3. Sampling stations

Sampling was performed inside and outside the Fe-enriched patch throughout the experiment. The positions of the sampling stations were based from surveys of the surface water SF_6 concentration (Watson et al., 2001). “In-stations” were situated in areas of high SF_6 concentration, whereas “out-stations” were within waters of the eddy that had a background SF_6 concentration. Vertical profiles were obtained from a 24 bottles (12-l) rosette coupled to a conductivity–temperature–depth (CTD) profiler (Sea-Birds Electronics SBE 911plus), and equipped with a Haardt fluorometer calibrated with chlorophyll *a* discrete samples (precision of $\pm 4\%$). Usually, samples were taken at about 12 different depths between 5 and 200 m. Samples for DIC, $f\text{CO}_2$ and nutrients were taken from the same cast at the same depths in order to obtain a coherent dataset.

2.4. Determination of DIC

The concentration of dissolved inorganic carbon was analysed on samples from regular CTD-casts inside and outside the patch, as well as on water from the ship's surface water supply every 7–8 min during the mappings of the patch. Samples from CTD casts were collected in 1-l glass bottles, which were kept cold before measurement. DIC was determined by the coulometric method of Johnson et al. (1993), as described by Stoll (1994).

A new coulometric cell was prepared on the discrete and online systems approximately every 12 h. Every coulometric cell was calibrated by Certified Reference Material (CRM) (batch #49). The accuracy and the precision of the system were evaluated by the measurement of two standards on each coulometric cell. Three to four replicate measurements for each sample and standard indicated a precision better than $1 \mu\text{mol kg}^{-1}$. The repeated measurement of the standard every 20 samples allowed us to correct for possible drift in the measurement. In the present paper, we only present data obtained with the cells with the optimal accuracy. The dissolved inorganic carbon data discussed below have an overall accuracy of $\pm 2 \mu\text{mol kg}^{-1}$.

2.5. Determination of $f\text{CO}_2$

Analysis of the fugacity of CO_2 was made from regular CTD-casts inside and outside the patch, as well as on water from the ship's surface water supply. The atmospheric CO_2 content was analysed in parallel in order to determine the CO_2 air–sea gradient. Marine air was collected through tubing from the crow's nest. Seawater was introduced at a rate of 3 l min^{-1} into a fast response equilibrator with a showerhead (adapted after Robertson et al., 1993; Bakker et al., 1997). Every 4 min an infrared LICOR 6262 analyser determined the molar fraction of CO_2 of a sample from the equilibrator headspace or from marine air. Samples from the equilibrator headspace and marine air were dried before analysis. The calibrated value for the mixing ratio of CO_2 in a dry sample ($x\text{CO}_2$ dry) was corrected to the mixing ratio of CO_2 in a wet sample for the equilibrator temperature and sea surface salinity, while using the infrared CO_2 analyser's (LI-COR

6262) reading for pressure. The formula for the water vapour pressure of seawater from the LI-COR 6262 handbook was used (LI-COR, 1996). The partial pressure of CO_2 ($p\text{CO}_2$) in the equilibrator was calculated from the mixing ratio in a wet sample and atmospheric pressure. The atmospheric pressure was determined using the atmosphere sensor of the ship's PODAS system, corrected to sea level, with a frequency of 1 min, an accuracy of 0.1 mbar and averaged to 10 min. A Pt-100 thermometer monitored the temperature of the water in the equilibrator. The $p\text{CO}_2$ in seawater was calculated by correction for warming of the water with the relationship by Takahashi et al. (1993). The $f\text{CO}_2$ was calculated, while using the equations by Weiss (1974). Standards of 295.1 and $406.1 \mu\text{mol CO}_2 \text{ mol}^{-1}$ (σ of 0.6 and $0.1 \mu\text{mol mol}^{-1}$, respectively), which had been calibrated against certified NOAA standards, were analysed every 45 min. The time delay between sampling and analysis was taken as 4 min for $f\text{CO}_2$ in air and surface water. The accuracy and precision of online surface water $f\text{CO}_2$ data were estimated as 1.0 and 0.6 μatm , respectively, as determined in a previous cruise (Bakker et al., 2001).

2.6. Determination of pH_T

Underway pH_T was determined using an automated marine pH sensor (AMpS), as previously described by Bellerby et al. (2002). In brief, the pH of seawater was measured from samples automatically drawn from the ship's continuous laboratory supply through a flow injection manifold coupled to a fibre optic array. The method of determination was dual spectrophotometric analysis of the seawater after the addition of a sulfonephthalein indicator. The background absorption spectrum of natural seawater was taken and an aliquot of thymol blue was injected into seawater enclosed in a flow cell. After the solution was fully mixed, spectral scans were taken along with solution temperature. The pH_T was estimated from the change in absorption between blanks and sample runs. The frequency of determination was 25 samples/h. The method has an on-line precision of better than 0.001 pH units and an estimated accuracy of better than 0.004 pH units (Bellerby et al., 2002).

2.7. Determination of nutrients and oxygen

Dissolved nutrients silicate, nitrate+nitrite ($\text{NO}_{3/2}$) and phosphate (PO_4^{3-}) were measured in all samples within 10 h after sampling, using a Technicon Autoanalyzer II system (Hartmann et al., 1997). All nutrient samples were analysed in duplicate, which gives a precision of $\pm 0.05 \mu\text{M}$ for nitrate+nitrite and silicate in the concentration range from 0 to $20 \mu\text{M}$ and $\pm 0.1 \mu\text{M}$ for the higher concentrations. For phosphate, the precision was $\pm 0.01 \mu\text{M}$. For calibration, three standards were run at the beginning and two standards at the end of each run, which give an accuracy of $\pm 0.1 \mu\text{M}$ for $\text{NO}_{3/2}$ and silicate and $\pm 0.01 \mu\text{M}$ for phosphate.

In the results and discussion below, we discuss the sum of nitrate and nitrite in order to consider the complete pool, which is the relevant entity when deriving uptake by plankton versus uptake of phosphate and silicate. Note that nitrite concentrations were always below $0.2 \mu\text{M}$.

Dissolved oxygen was determined (De Baar, 2001) with the method of Pai et al. (1993) with an estimated accuracy of $\pm 1 \mu\text{mol kg}^{-1}$. The complete dataset for all parameters discussed in this paper is available from the authors Y. Bozec and H.J.W. de Baar at NIOZ and can also be found at the cruise website <http://www.pangaea.de/PangaVista?query=eisenex>.

3. Results and discussion

3.1. Experimental site study

The physical, biological and chemical properties of the eddy were determined in a fine-scale hydrographical survey before the iron addition. The purpose of this survey was to measure the “natural” conditions of the eddy relative to which any subsequent change would occur. The results of the surface survey are given in Table 1 along with the results from three other iron enrichment experiments. The carbonate system in surface waters of the eddy had quite uniform properties. Surface water properties were representative of the HNLC regions in the Southern Ocean and were rather similar to the properties encountered in the SOIREE experiment (61°S , 140°E), a previous iron enrichment experiment in a different sector of the Southern Ocean (Boyd et al., 2000). The DIC, $f\text{CO}_2$ and pH_T in the eddy’s surface waters were $\text{DIC}=2131 \pm 2 \mu\text{mol kg}^{-1}$, $f\text{CO}_2=360 \pm 2 \mu\text{atm}$ and $\text{pH}_\text{T}=8.076 \pm 0.001$ (Table 1). These data provide baseline values for the carbonate system, relative to which the changes due to the iron addition were determined.

3.2. Meteorological and hydrographical forcing

During EisenEx, the development of the algal bloom and thus the algal carbon uptake were strongly

Table 1

The physical, chemical and biological properties of the surface waters before iron addition during the four Fe-enrichment experiments and their standard deviations on the means (\pm)

Parameters	IronEx I	IronEx II	SOIREE	EisenEx
Temperature ($^\circ\text{C}$)	22.9 ± 0.2	25.2 ± 0.5	2.0 ± 0.5	3.5 ± 0.2
Salinity	35.36 ± 0.01	35.07 ± 0.03	—	33.80 ± 0.01
Chlorophyll <i>a</i> ($\mu\text{g l}^{-1}$)	0.24 ± 0.02	0.3 ± 0.02	0.25 ± 0.03	0.48 ± 0.03
DIC ($\mu\text{mol kg}^{-1}$)	2044 ± 3	2051 ± 5	2136.6 ± 2.7	2131 ± 2
$f\text{CO}_2$ (μatm)	471 ± 7	538 ± 12	350 ± 2	360 ± 2
pH^a	8.253 ± 0.008	8.275 ± 0.016	—	8.076 ± 0.001
NO_3^- (μM)	10.8 ± 0.4	10.4 ± 0.3	25.4 ± 0.3	23.5 ± 0.1
PO_4^{3-} (μM)	0.92 ± 0.02	0.80 ± 0.03	1.42 ± 0.02	1.60 ± 0.01
SiO_2 (μM)	3.9 ± 0.1	5.0 ± 0.2	9.5 ± 0.4	14.2 ± 0.1
O_2 (μM)	230 ± 1	220 ± 1	—	350 ± 1
Fe (nM)	~ 0.06	~ 0.02	~ 0.08	~ 0.08

From Martin et al. (1994), Watson et al. (1994), Coale et al. (1996), Cooper et al. (1996), Steinberg et al. (1998), Boyd et al. (2001), Bakker et al. (2001) and this study.

^a pH has been normalized to a temperature of 4°C .

influenced by physical processes. The average wind speed of 8.0 m s^{-1} encountered in the first week of the experiment was distinctly lower than average values in this region (Dentler, 2001). The wind and mixing conditions of the second and third week of the experiment were typical for the region of the ACC (Mitchell et al., 1991) with alternating periods of medium and strong storms. The average wind speeds were 10.4 and 12.1 m s^{-1} , respectively. Due to horizontal dispersion, the patch, marked by the inert tracer SF_6 , increased from initially 50 km^2 to about 950 km^2 at the time of our last mapping on days 17–18 of the experiment (Watson et al., 2001). Very likely, the succession of high winds promoting deep mixing, and sunny and calm days (with an average wind speed around 5 m s^{-1}) allowing development of a strong stratification, were an important factor in the development of the phytoplankton in the centre of the patch (Gervais et al., 2002) and thus in the algal uptake of inorganic carbon and nutrients.

3.3. Inorganic carbon uptake during EisenEx

The response of the carbonate system to the iron enrichment within the patch was measured for 21 days following the first addition. The changes in DIC, $f\text{CO}_2$ and pH_T were determined relative to measurements in the eddy before the experiment and to measurements outside of the patch during the experiment.

Algal response to the iron addition was characterized by an increase in chlorophyll *a* from $0.50 \mu\text{g l}^{-1}$ on day 0 to 0.75 g l^{-1} on day 3. On day 4 after the iron enrichment, a difference of surface water DIC between outside and inside the patch (ΔDIC) of $4 \mu\text{mol kg}^{-1}$ was observed in EisenEx (Fig. 1A), which

is similar to that in SOIREE (Bakker et al., 2001), but is two to three times lower than that during IronEx II 2 days after iron release (Cooper et al., 1996; Steinberg et al., 1998). The response was slower and initial changes in the carbonate system occurred later during both EisenEx and SOIREE than during the IronEx II

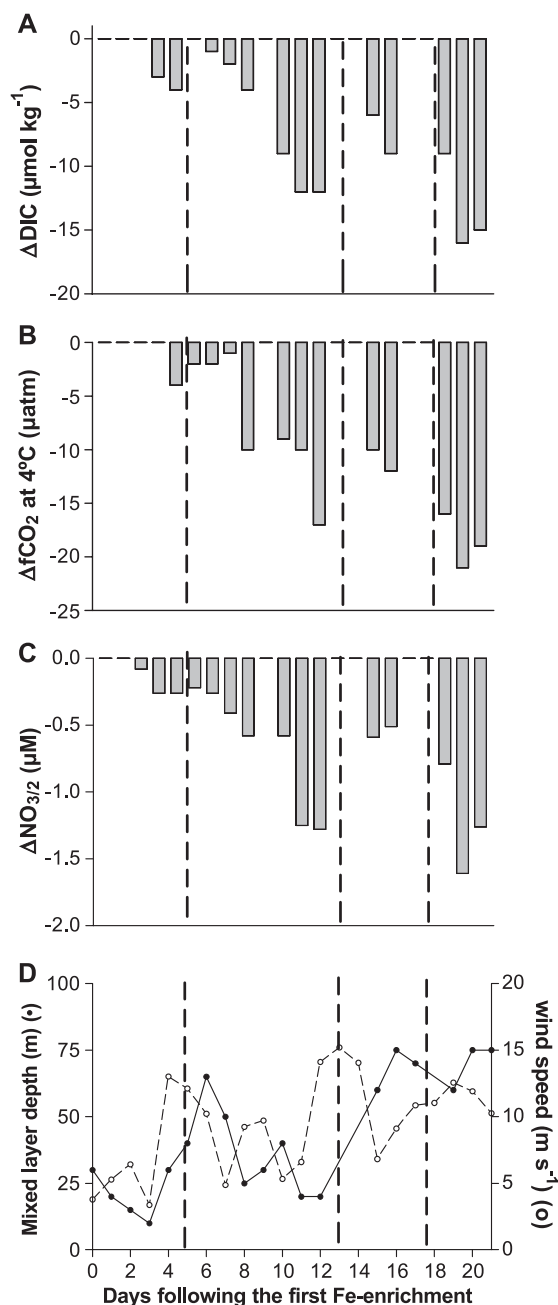


Fig. 1. Daily changes (Δ) in surface DIC (A), $f\text{CO}_2$ (normalized at a temperature of 4°C) (B) and nitrate (C) between inside the patch and outside the patch as well as changes in the mixed layer depth (—) and daily average wind speed (---) (D) during the experiment. For each day, the Δ for DIC and nitrate correspond to the difference between the CTD data at the in station and the CTD data at the corresponding out station. For $f\text{CO}_2$, the Δ were computed from surface measurement at the in station and surface measurement at the corresponding out station. For the wind speed, the height of the anemometer was 38 m and wind speeds have been corrected to 10 m height using the relationship by Johnson (1999). The dashed lines indicate the two severe storms on days 4–5 and 12–13 as well as the strong gale on days 17–18.

experiment. Algal carbon uptake was observed within two days of the first iron infusion in IronEx I and II (Watson et al., 1994; Cooper et al., 1996; Millero et al., 1998; Steinberg et al., 1998), whereas it was only observed after 4–5 days during EisenEx and SOIREE. The low temperature of the Southern Ocean waters was deemed to be responsible for this slow response in SOIREE (Boyd et al., 2000) and this might also be the case for EisenEx (Table 1).

A severe storm (maximum wind speed of 25.2 m s^{-1}), after 5–6 days decreased ΔDIC in the patch center from 5 to $2 \mu\text{mol kg}^{-1}$ by mixing up of water with higher DIC concentrations from below (as mixed layer depths increased from around 25 m to about 60

m) and by horizontal dispersion of the patch. On days 10 and 12, rapid carbon uptake was observed, ΔDIC was 9 and $12 \mu\text{mol kg}^{-1}$ (Fig. 1A), respectively, in a mixed layer of 20 m (Figs. 1D and 2A). On day 12, this ΔDIC was related with an equivalent increase in oxygen concentrations of $10 \mu\text{M}$ (Fig. 2B) and a decrease in $\text{NO}_{3/2}$ of $1.3 \mu\text{M}$ (Fig. 1C). The iron was initially injected at $16 \pm 2 \text{ m}$ depth in the initially shallow surface mixed layer of 30 meters. Thus, the storm after 5–6 days may have improved the iron availability for algae below the shallow surface layer. The twofold increase in chlorophyll *a* concentration after 12 days (Riebesell, personal communication) showed that an algal bloom had developed in the

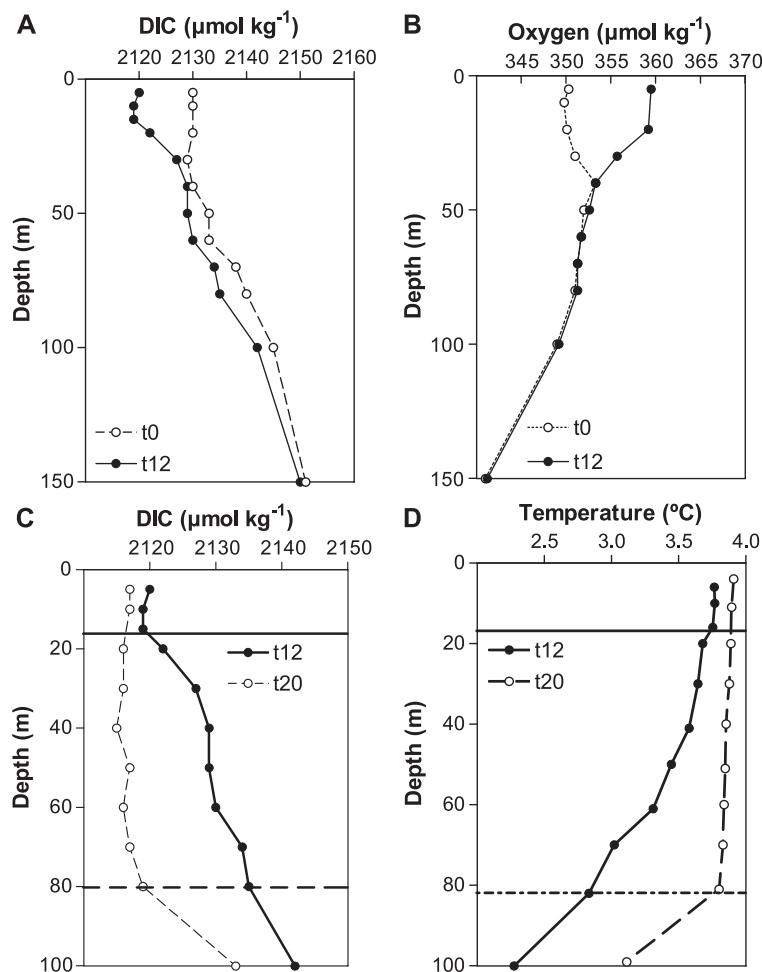


Fig. 2. Upper panel: DIC (A) and O_2 (B) profiles on days 0 and 12. Bottom panel: changes in the mixed layer depth evident from DIC (C) and temperature (D) profiles on days 12 and 20.

calm and sunny conditions and was responsible for the DIC and $\text{NO}_{3/2}$ decrease (Fig. 1A and C) and the increase in oxygen concentrations (Fig. 2B). The ΔDIC decrease to $6 \mu\text{mol kg}^{-1}$ on day 15 is related to the second severe storm (maximum wind speed of 26.9 m s^{-1}), that occurred on day 13 (Fig. 1D). Twenty days after the first Fe-infusion, a maximum $\Delta\text{DIC}=15 \mu\text{mol kg}^{-1}$ was observed in an 80-m deep mixed layer (Fig. 2C and D) with a concomitant maximum $f\text{CO}_2$ decrease of $23 \mu\text{atm}$ (Fig. 1B) and an

increase in pH_T of 0.025 units compared to the outside patch. The concentrations of DIC below the euphotic zone both inside and outside the patch remained constant during the experiment with values at 150 and 200 m of 2150 and 2160 $\mu\text{mol kg}^{-1}$, respectively (Fig. 3).

Although changes in DIC and $f\text{CO}_2$ did not occur linearly throughout the experiment, they were well correlated during the 21 days of experiment (Fig. 1) (the linear regression of surface water changes in

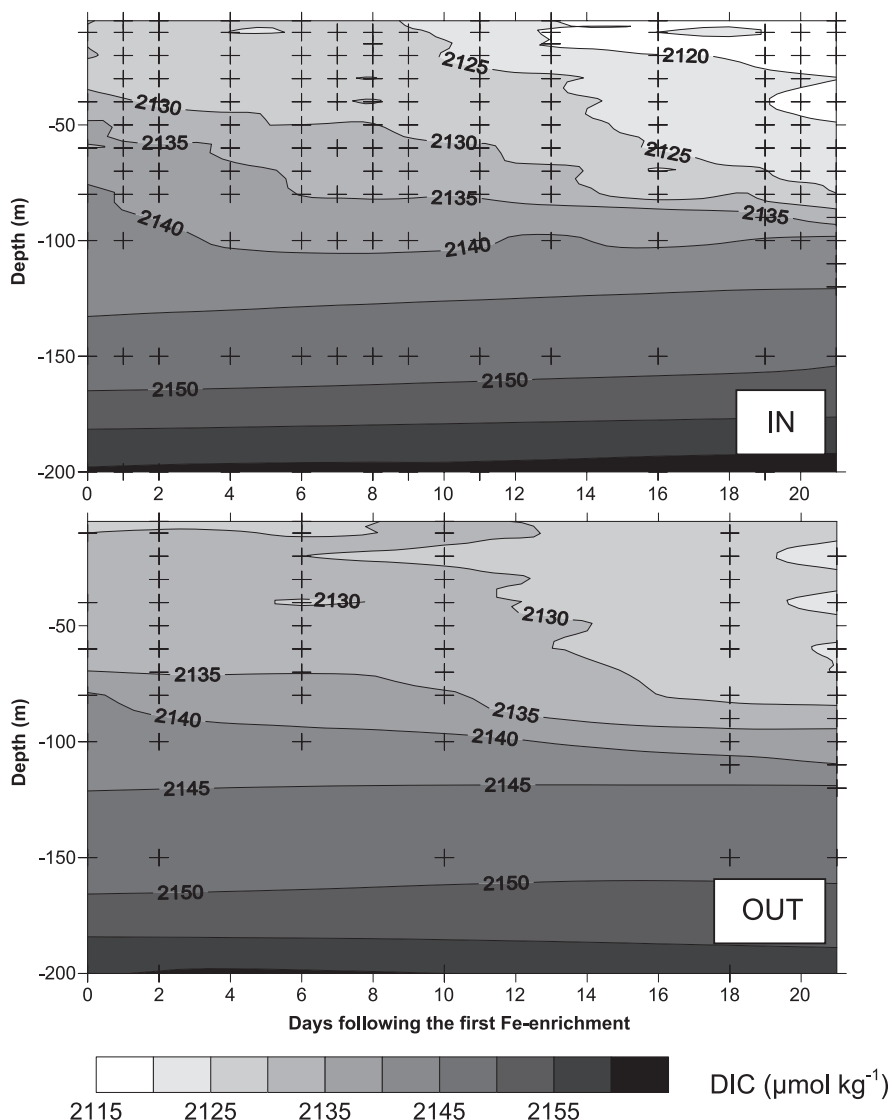


Fig. 3. Contour plots for DIC evolution inside and outside the patch in the first 200 m of the water column. Crosses represent the sampling frequency in time and depth.

$f\text{CO}_2$ relative to average DIC in the mixed layer for each day gives $r^2=0.87$, $n=15$). The variable DIC and $f\text{CO}_2$ uptake in this dynamic environment differ from the almost linear DIC and $f\text{CO}_2$ uptake during IronEx II (Cooper et al., 1996; Steinberg et al., 1998) and SOIREE (Bakker et al., 2001). The maximum DIC and $f\text{CO}_2$ uptake during IronEx II were $27 \mu\text{mol kg}^{-1}$ and $70\text{--}90 \mu\text{atm}$, respectively, after 6–9 days of significant carbon uptake over the 25-m deep mixed layer (Table 2) (Cooper et al., 1996; Steinberg et al., 1998). These changes were two to three times those of $15\text{--}18 \mu\text{mol kg}^{-1}$ and $32\text{--}38 \mu\text{atm}$ after 13 days of SOIREE, which corresponded to 8–9 days of significant carbon uptake over the upper 50 m (Bakker et al., 2001).

In addition to the daily measurements taken inside and outside the patch, seven surface water mappings were completed during the 21 days of the experiment, in order to study the spatial distribution of the biogeochemical response to the Fe-enrichment. On days 17 and 18, a final grid study was conducted for 34 h in the fertilized waters, clearly visible from DIC, $f\text{CO}_2$, chlorophyll *a* and SF_6 in surface water (Fig. 4). During this surface survey, DIC (Fig. 4A) and SF_6 (Fig. 4D) were inversely related. The crossings of the patch with the highest SF_6 concentrations corresponded to low DIC, whereas the background SF_6 concentrations were related to outside patch DIC concentrations. The lowest values in DIC were concomitant with $f\text{CO}_2$ minima (Fig. 4B). The maximum uptake of DIC and $f\text{CO}_2$ during this grid study were $8\text{--}9 \mu\text{mol kg}^{-1}$ and $17\text{--}20 \mu\text{atm}$,

respectively. These values are in good agreement with DIC and $f\text{CO}_2$ at the inside station on day 19 and the outside station on day 20 (Fig. 1A and C). The changes in the carbonate system directly correspond to the growth of phytoplankton as indicated by the corresponding chlorophyll *a* increases in Fig. 4C.

3.4. Relationship of changes in CO_2 to nutrients

During EisenEx, the iron addition promoted an increase in chlorophyll *a* (Fig. 4C) and a decrease in DIC, nitrate (Fig. 1C) and phosphate (Table 2), indicating that iron limits algal growth and nutrient utilisation. While a significant increase in diatom abundance was observed in the patch by the end of the experiment, a decrease of silicate occurred both inside and outside the patch (Fig. 5) (Assmy et al., 2001). The decrease in silicate concentrations in the surface waters was slightly higher outside patch than inside patch. While the weakly silicified *Pseudonitzschia* became the dominant diatom during EisenEx, the highly silicified *Fragilaropsis kerguelensis* dominated the SOIREE bloom. As a consequence, the silicate uptake of $2.5 \mu\text{mol l}^{-1}$ measured during SOIREE (Boyd et al., 2000) was much larger than during our experiment. Takeda (1998) observed similar uptake of silicate in incubations bottles for both, iron limited and iron enriched cultures of *Pseudonitzschia* diatoms and concluded that the iron nutritional status of the diatoms appears to affect silicate utilization physiologically. Hutchins and Bruland (1998) found ratios of Si/diatoms per cell, which were 2.9 times higher for

Table 2

Maximum changes in the chemical parameters during IronEx I (3 days after first Fe-addition in a mixed layer of 35 m depth), IronEx II (8 days after the first iron addition in a mixed layer of 50 m depth), SOIREE (13 days after the first Fe-addition in upper 50 m depth) and EisenEx (on t18 in a mixed layer of 60 m depth; except for O_2 on t12 in 20 m depth) as well as the iron level reached after the first fertilisation

Parameters	IronEx I	IronEx II	SOIREE	EisenEx
Chlorophyll ($\mu\text{g l}^{-1}$)	$+0.41 \pm 0.02$	$+3.90 \pm 0.02$	$+3.11 \pm 0.02$	$+2.32 \pm 0.03$
DIC ($\mu\text{mol kg}^{-1}$)	-6 ± 2	-27 ± 2	-18 ± 3	-15 ± 2
$f\text{CO}_2$ (μatm)	-13 ± 6	-73 ± 6	-38 ± 2	-23 ± 2
pH	—	—	—	$+0.025 \pm 0.001$
O_2 (μM)	$+2.8 \pm 1$	$+32 \pm 1$	—	10 ± 1
NO_3^- (μM)	-0.7 ± 0.2	-4.0 ± 0.2	-3.0 ± 0.3	-1.6 ± 0.1
PO_4^{3-} (μM)	-0.02 ± 0.02	-0.25 ± 0.02	-0.20 ± 0.02	-0.16 ± 0.01
SiO_2 (μM)	-0.02 ± 0.02	-4.0 ± 0.2	-2.5 ± 0.4	≈ 0
Fe (nM)	≈ 4	≈ 2	≈ 3.8	4.5 ± 3.0

Signs “ \pm ” are followed by the standard deviations on the means for each parameter. From Martin et al. (1994), Watson et al. (1994), Coale et al. (1996), Cooper et al. (1996), Steinberg et al. (1998), Boyd et al. (2000), Bakker et al. (2001) and this study.

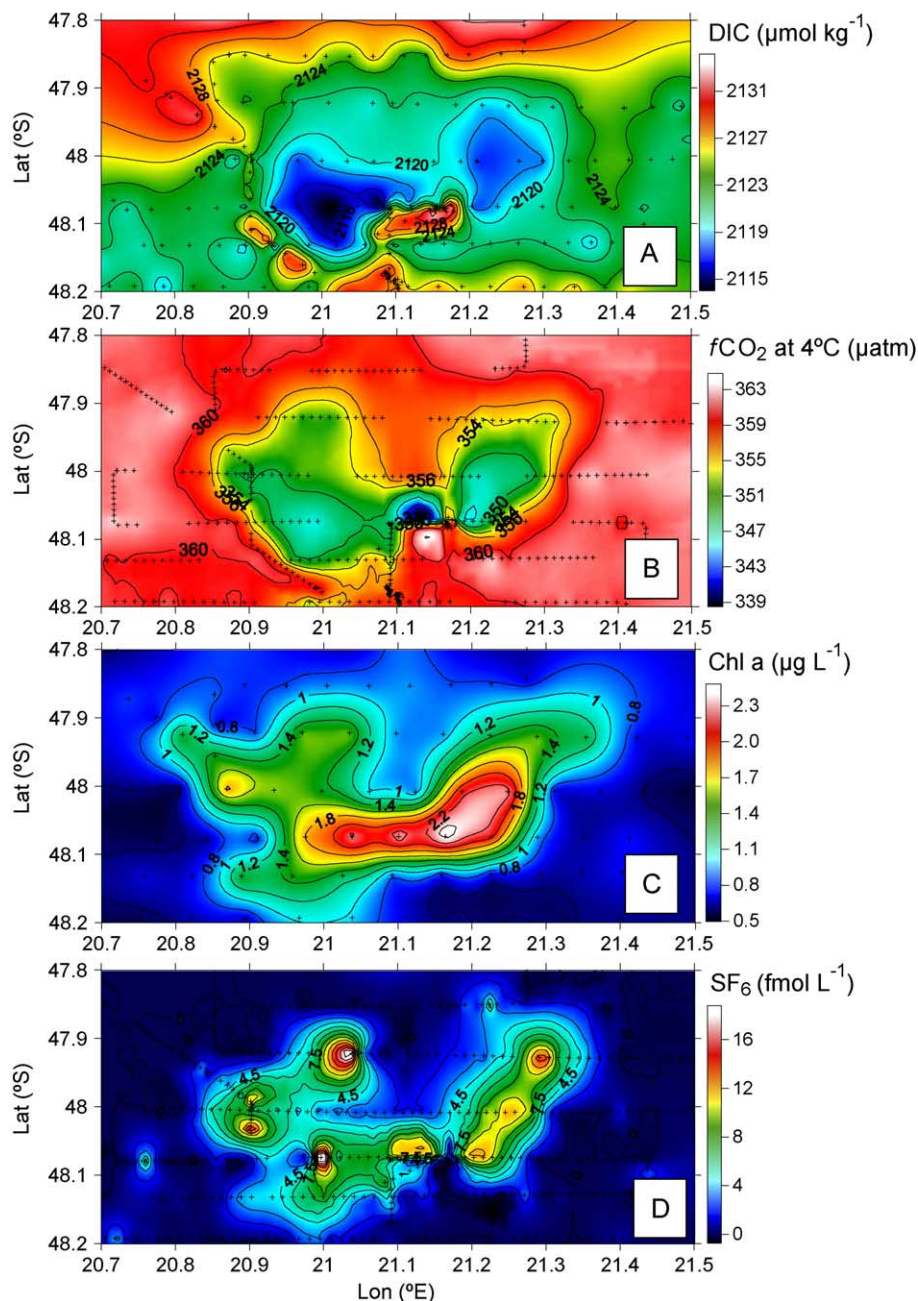


Fig. 4. Shape and location of the patch on day 18 from surface DIC (A), $f\text{CO}_2$ (normalized at a temperature of 4°C) (B) and SF_6 (D) data measured continuously, and from chlorophyll *a* (C) measured on CTD samples. The surface water measurements for each parameter were interpolated at a 0.5° latitude by 0.5° longitude grid by kriging. Crosses are the locations of the surface samples for each parameter.

diatoms growing under Fe-limited conditions than in Fe-replete conditions. Recent results from Brzezinski et al. (2003) point to the operation of an efficient

silicate pump. This “pump” for diatoms growing under low Fe-concentrations in the Southern Ocean enriches particles in silica relative to organic matter

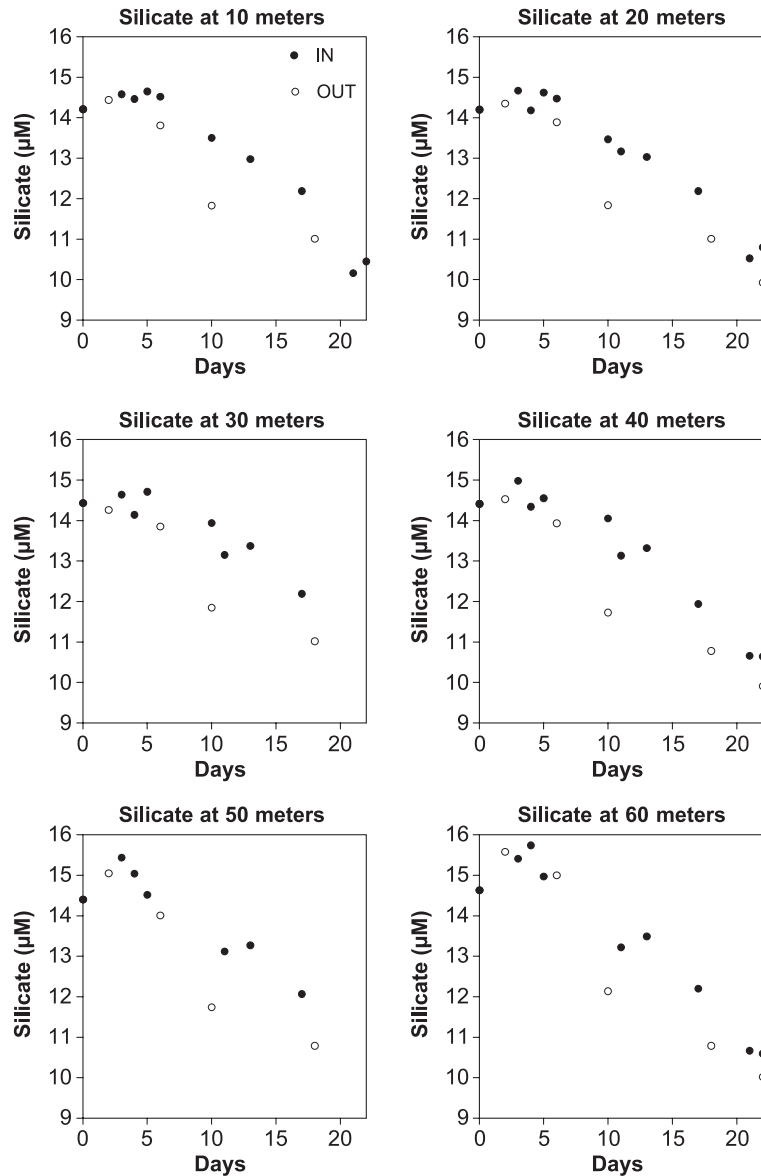


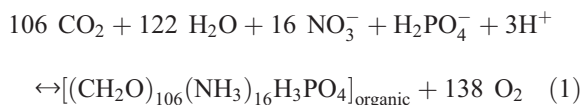
Fig. 5. Evolution of silicate inside (●) and outside (○) the Fe-enriched patch at 10, 20, 30, 40, 50 and 60 m depth.

prior to their export into deeper waters. This could explain the relatively large uptake of silicate observed outside the EisenEx patch and would lead to more silicified, faster sinking diatoms under iron limitation than in iron enriched waters (Hutchins and Bruland, 1998; De La Rocha et al., 2000). Indeed, Waite and Nodder (2001) reported sinking rates of diatoms significantly lower inside the patch than outside the patch during the SOIRE experiment. These authors

also reported that the primary bloom species reduced their sinking rates most markedly within the patch, showing a decrease of 87% of initial sinking rates after 13 days. On one hand the addition of iron enhanced diatoms growth and therefore the CO_2 uptake from the atmosphere, whereas on the other hand, the production of less silicified diatoms decreased their sinking rates and therefore diminished the CO_2 export to the deeper layers. Thus, during in-

situ Fe-enrichment experiments, the iron addition caused opposing effects on the uptake and export of CO₂ to the deeper layers.

The relationship between changes in the inorganic carbonate system and nutrients during photosynthesis is frequently examined using the Redfield equation (Redfield et al., 1963).



Large deviations from the Redfield proportions have been observed for Antarctic diatoms growing under suboptimal conditions of Fe supply (De Baar et al., 1997). During EisenEx, the least square fits of the data inside the Fe-enriched patch give N/P=12, C/P=82, C/N=5.9, C/Si=2.9 and N/Si=0.5 (Fig. 6). The N/P, C/P and C/N ratios are lower than the average oceanic values of 16, 106 and 6.6, but comparable to the ratios found in IronEx II (Steinberg et al., 1998) and during spring 1992 at 50°S, 6°W (De Baar et al., 1997) (Table 3). Takahashi et al. (1985) pointed out that Eq. (1) assumes that the organic carbon is in the form of carbohydrate, while many organisms, such as diatoms, produce a large quantity of lipid material. Similarly, based on investigations of organic matter containing a large quantity of lipid material, Hedges et al. (2002) reported C/N ratios of approximately 6.0 in the Southern Ocean. Therefore, formation of lipids will lower the carbon to nutrient and the carbon to oxygen ratio. The C/P, C/N and N/P ratios reported in this study, as well as studies by De Baar et al. (1997) and Steinberg et al. (1998), are lower than Redfield ratios, presumably because diatoms are responsible for a large part of the algal growth. Stoll et al. (2002) reported a similar value of 0.5 for N/Si (Table 3) in a diatom bloom in the Polar front zone. These findings support strong diatom growth as a possible cause of the lower values determined in some oceans for C/P, C/N and N/P ratios (Takahashi et al., 1985; De Baar et al., 1997; Steinberg et al., 1998). Moreover, lower C/N and C/P ratios are also commonly observed in an early stage of a bloom, as a consequence of luxury consumption of nitrate and phosphate (Droop, 1973; Thomas et al., 1999). Relatively small changes in DIC, NO_{3/2} and PO₄³⁻ outside of the patch,

together with the low abundance of diatoms (Assmy et al., 2001) suggest that no bloom started there. Thus, the lower ratios obtained during this study inside the patch could be a combination of high production of diatoms together with luxury consumption in the early stage of a phytoplankton bloom induced by iron-enrichment. Outside the patch some diatom growth under iron limited conditions could be responsible for the Si-uptake, which was slightly higher than inside the patch.

3.5. Effect of air–sea fluxes on Redfield ratios

As mentioned above, several severe storms with high wind speed occurred during our experiment and have influenced the CO₂ air–sea exchange. It is important to study the impact of this exchange on the observed DIC changes and the carbon to nutrient ratios.

The flux (F) of CO₂ across the air–sea interface can be calculated from the relation:

$$F = k.s.(f\text{CO}_{2\text{water}} - f\text{CO}_{2\text{air}}),$$

in which k is the gas transfer velocity, s the solubility of CO₂ calculated after Weiss (1974), $f\text{CO}_{2\text{water}}$ the fugacity of CO₂ in the surface water and $f\text{CO}_{2\text{air}}$ the fugacity of CO₂ in air. The main factor influencing k is turbulence at the air–sea interface that is mainly generated by wind stress; thus, k is usually parameterised as a function of wind speed. Several algorithms have been proposed for the k -wind speed relationship. We applied two commonly used algorithms (Liss and Merlivat, 1986; Wanninkhof, 1992) and two recently proposed ones (Wanninkhof and Mc Gillis, 1999; Nightingale et al., 2000), here after referred to as L&M86, W92, W&Mc99 and N2000, respectively. We decided to use the four relationships because even the latest experiments using the most recent tracer techniques (Wanninkhof and Mc Gillis, 1999; Nightingale et al., 2000) could not reliably distinguish, which was the optimal relationship. Moreover, the W&Mc99 relationship is constrained by k measurements up to wind speeds of 15 m s⁻¹ and could achieve a better calibration span for the wind speed measured during our experiments. It will be interesting to compare the results from W&Mc99 to L&M86 for EisenEx.

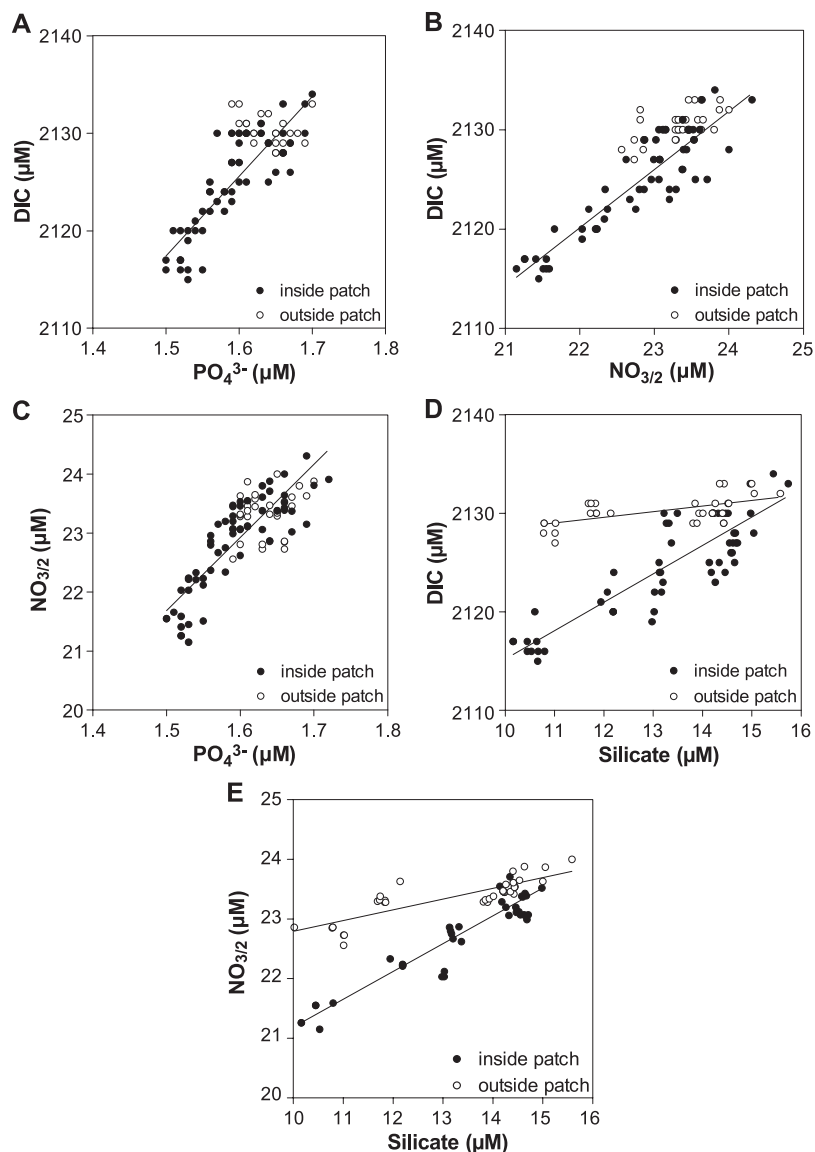


Fig. 6. The changes in DIC, $\text{NO}_{3/2}$, PO_4^{3-} and silicate for individual CTD samples in the upper 60 m inside (●) and outside (○) the iron enriched patch during the experiment. Fits inside the patch are: (A) $\text{DIC} = 81.5 \text{ PO}_4^{3-} + 1995.4$, $r^2 = 0.72$, $n = 57$; (B) $\text{DIC} = 5.9 \text{ NO}_{3/2} + 1990.3$, $r^2 = 0.81$, $n = 57$; (C) $\text{NO}_{3/2} = 12.0 \text{ PO}_4^{3-} + 3.65$, $r^2 = 0.73$, $n = 61$; (D) $\text{DIC} = 2.935 \text{ Si} + 2085.6$, $r^2 = 0.76$, $n = 57$; and (E) $\text{NO}_{3/2} = 0.476 \text{ Si} + 16.394$, $r^2 = 0.88$, $n = 43$.

Outside the patch the $f\text{CO}_2$ in surface water and air approximately stayed in equilibrium during the experiment with an average value of $362 \mu\text{atm}$.

Inside the patch, we calculated F using the four formulations and the wind speed corrected to 10-m height. For each day, a flux was calculated using an average daily wind speed, an average $f\text{CO}_2$ in the

surface water and a constant value of $362 \mu\text{atm}$ for $f\text{CO}_{2\text{air}}$. The values calculated using the four different formulations range between -0.09 and $-9.93 \text{ mmol m}^{-2} \text{ day}^{-1}$. Once integrated across the mixed layer and corrected for density, values range from -0.02 to $-0.33 \mu\text{mol kg}^{-1} \text{ day}^{-1}$, using L&M86 and W&Mc99, respectively. The average

Table 3

Slopes of linear regressions of nutrients observed during IronEx II (Steinberg et al., 1998), a diatom bloom in the Antarctic Circumpolar Current at 50°S, 6°W (De Baar et al., 1997) and EisenEx, compared to the Redfield ratios (Redfield et al., 1963)

In patch	EisenEx	IronEx II	Spring 1992 (50°S, 6°W)	Redfield ratio
$\Delta C/\Delta P$	82±5	90±5	86	106
$\Delta C/\Delta N$	5.9±0.2	6.2±0.2	4.7–6.1	6.6
$\Delta N/\Delta P$	12.0±0.2	14.3±0.2	14.2	16
$\Delta C/\Delta Si$	2.9±0.3	5.1±0.3	–	–
$\Delta N/\Delta Si$	0.5±0.1	–	0.11–0.15	–

It was not possible to derive a similar trend for O₂ versus DIC consumption, because of a lack of consistent O₂ data for the whole course of the EisenEx experiment.

fluxes of carbon from the atmosphere integrated across the mixed layer were -0.05 , -0.08 , -0.10 and -0.07 $\mu\text{mol kg}^{-1} \text{ day}^{-1}$ for L&M86, W92, W&Mc99 and N2000, respectively. For the 21 days of experiment, the total flux of carbon from the atmosphere into the mixed layer, where the DIC uptake occurred, ranged between 1.0 and 2.0 $\mu\text{mol kg}^{-1}$ using L&M86 and W&Mc99, respectively. These values are of the same order of values as the accuracy of the DIC measurements. We corrected the ΔDIC measured at every station using the daily air–sea fluxes calculated inside the patch and integrated across the mixed layer at the corresponding day. Plots (not shown) similar to Fig. 6 using DIC corrected for the air sea exchange, changed the ratio in Table 3 as follows: C/P from 81.6 to 82.0, C/N from 5.9 to 6.1 and C/Si from 2.9 to 3.0. These changes are smaller than the uncertainties on these ratios and do not alter any of our conclusions. The air–sea exchange of CO₂ had a negligible impact on the carbon to nutrient ratios.

3.6. Overall biological uptake

The high wind velocity leading to the deepening of the wind mixed layer is deemed to be detrimental to the average light climate for the growth rate of the phytoplankton (De Baar and Boyd, 2000; Lancelot et al., 2000; Van Oijen et al., 2004). This, in combination with the severe dilution of the patch with ambient waters, is likely to be the major reason, why the overall removal of DIC and major nutrients was on the one hand significant, but on the other hand by no

means utilizing the full growth potential of the available major nutrient stocks. By considering the area covered by the Fe-enriched surface waters, we assessed the total biological C uptake for the whole patch.

From the mapping on day 18 (Fig. 4), we assume that the area where the highest ΔDIC was observed covers approximately one-fourth (or 250 km²) of the patch. We considered that the ΔDIC of 15 $\mu\text{mol kg}^{-1}$ observed on day 20 was only situated in these 250 km² of the patch centre. For the rest of the patch (approximately 750 km² on day 20), we assumed that the ΔDIC was closer to 10 $\mu\text{mol kg}^{-1}$, according to the results of the last mapping on day 18. These changes were observed in the mixed layer of 80 m. Therefore, the total C uptake in the centre of the patch was 1232 mmol m⁻² and for the rest of the patch 1026 mmol m⁻² on day 20. These results are in good agreement with the cumulative ¹⁴C primary production of approximately 1000 mmol m⁻² integrated over the same depth at the same date, which exceeded primary production in non fertilized water by a factor three (Gervais et al., 2003). In total on day 20, the ΔDIC observed in the Fe-enriched waters was equivalent to a C uptake of 1.08×10^9 mol C or 1.3×10^{10} g C. This can be compared to the amount of iron added during the experiment. In total, 4.2×10^4 mol of Fe were added, which gives a ratio C-uptake versus Fe (C/Fe) of 2.5×10^4 mol mol⁻¹. During the SOIREE experiment, the C uptake was 1.1×10^8 mol C after 13 days of experiment (Bakker et al., 2001), which is tenfold lower than during EisenEx after 20 days. Thus, although the ΔDIC observed during the EisenEx experiment was not that extensive compare to the previous iron enrichment experiments, the large dispersion of the patch caused a total C-uptake for the whole patch that was larger than during previous Fe fertilization experiments.

One major consequence of the stormy conditions is the increase of the mixed layer depth that might induce a light limitation. In the Southern Ocean, optimal light conditions prevail during austral summer (December–January), when incoming solar irradiance is most intense, day length is longest, and the wind mixed layer is the shallowest due to relatively low wind velocities. During the recent SEEDS experiment in the Subarctic Pacific Ocean, the very shallow and stable wind mixed layer of 10 m depth allowed a

complete removal of 20 μM of nitrate within 2 weeks, because of the optimum light availability. However, the nitrate uptake remained confined to a small area (Tsuda et al., 2003). This illustrates the importance of weather conditions on the key factors, such as light conditions and iron availability, for phytoplankton growth and the concomitant CO_2 uptake during Fe-enrichment experiments.

4. Conclusion

The EisenEx experiment demonstrated that iron is a limiting nutrient for phytoplankton growth in the Southern Ocean. We observed an uptake of CO_2 within 5 days after the first Fe-addition. This uptake was strongly influenced by the changes in mixed layer depth due to the succession of storms and calm weather during the experiment. A maximum uptake of DIC of 15 $\mu\text{mol kg}^{-1}$ in a mixed layer of 80 m depth occurred 20 days after the first Fe-infusion, and was concomitant with a maximum uptake of $f\text{CO}_2$ of 23 μatm and an increase in pH of 0.025 units. The uptake of CO_2 and nutrients were well correlated suggesting that algal growth was responsible for the decrease in CO_2 in the surface waters of the patch compared to the outside patch. A similar uptake of silicate was observed inside and outside the patch. The presence of diatoms growing under Fe-depleted conditions outside the patch might be responsible for substantial silicate uptake outside the patch.

In the surface waters of the patch, we found values of 82, 5.9, 12, 2.9 and 0.5 for the ratios C/P, C/N, N/P, C/Si and N/Si, respectively. Those values are in agreement with values reported for diatom blooms in the Southern Ocean (Fanning, 1992; De Baar et al., 1995). The sudden availability of iron in surface waters rich in major nutrients might have created a state of luxury consumption, as suggested by Droop (1973). This effect in combination with the strong growth of diatoms might explain the low ratios calculated. The effect of air–sea exchange of CO_2 on DIC uptake was small and did not significantly affect the values for these ratios.

Overall, the observed changes in the water column in DIC due to Fe fertilization were relatively modest but once integrated for the whole patch, equivalent to a significant uptake of 1.1×10^9 mol C and a C/Fe

ratio of 2.5×10^4 mol mol $^{-1}$. In that respect, the EisenEx experiment has underlined the major impact of weather conditions on factors such as iron availability and light conditions, which are directly responsible for the overall CO_2 uptake during in-situ Fe-enrichment.

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